ON THE MECHANISM OF THE FORMATION OF OZONIDES OF THE ALKALI METALS

I. I. Vol'nov, V. N. Chamova, and E. I. Latysheva

In the articles [1, 2], the following scheme of the mechanism of the formation of alkali metal ozonides in the reaction of an ozone-oxygen mixture with solid alkalies was cited:

\[
2\text{MOH} + 2\text{O}_3 \rightarrow 2\text{MOH}_2\text{O}_3 \quad (1)
\]

\[
2\text{MOH}_2\text{O}_3 + 2\text{O}_3 \rightarrow 2\text{MO}_2 + 2\text{H}_2\text{O} + 2\text{O}_2 \quad (2)
\]

\[
2\text{H}_2\text{O} \rightarrow \text{H}_2\text{O} + 1.5\text{O}_3 \quad (3)
\]

\[
\text{MOH} + \text{H}_2\text{O} \rightarrow \text{MOH}_2\text{H}_2\text{O} \quad (4)
\]

\[
3\text{MOH} + 4\text{O}_2 \rightarrow 2\text{MO}_2 + \text{MOH}_2\text{H}_2\text{O} + 3.5\text{O}_2 \quad (5)
\]

An estimate of the values of the standard thermodynamic functions of reaction (5) for KOH gives: \(\Delta H = -134 \text{ kcal/mole}\), \(\Delta F = -125.9 \text{ kcal/mole}\), and \(\Delta S = -27.4 \text{ entropy units}\).

This scheme has not been demonstrated experimentally. It is based on two hypotheses — on the hypothesis of formation of an unstable complex of the hydroxides of sodium, potassium, rubidium, and cesium (but not lithium) with the ozone molecule \(\text{MOH} \cdot \text{O}_3\) according to reaction (1) and on the hypothesis of the participation of the \(\text{HO}_2\) radical in the formation of ozonides of these elements according to reaction (2). The authors of the article [3] exclude the primary displacement of the hydroxyl of MOH by ozone, since this contradicts the thermodynamic data. An estimate of \(\Delta H\), \(\Delta F\), and \(\Delta S\), for example, of the reaction \(\text{KOH} + \text{O}_3 \rightarrow \text{KO}_3 + \text{OH}\), leads to the values \(+15.9 \text{ kcal/mole}\), \(+16.4 \text{ kcal/mole}\), and \(-3.2 \text{ entropy units}\), respectively, whereas the value of \(\Delta H\) of reaction (2) is approximately \(-54 \text{ kcal/mole}\). The hydroxide oxygen should participate in the formation of the radical \(\text{HO}_2\) according to the scheme:

\[
\text{MOH} + \text{O}_2 \rightarrow \text{MOH} \cdot \text{H}_2\text{O} \rightarrow \text{HO}_2 + \text{O}_2
\]

The only experimentally demonstrated reactions in the scheme cited above are reaction (3), which follows from the data of [4], and reaction (4). With respect to the latter, however, it should be mentioned that at the temperatures at which ozonation was conducted (\(-15^\circ\) for KOH and \(-60^\circ\) for NaOH) and at the water concentration that is created in the system according to reaction (3), the monohydrate \(\text{MOH} \cdot \text{H}_2\text{O}\) can exist in a mixture with anhydrous MOH [5]. Consequently, the gross reaction (5) does not correspond to that which is observed experimentally. Equation (5) should have been written as follows:

\[
n\text{MOH} + m\text{O}_2 \rightarrow (n - 3)\text{MOH} + \text{MOH} \cdot \text{H}_2\text{O} + 2\text{MO}_2 + (1.5m - 2.5)\text{O}_2
\]

According to Eq. (5), under the assumption of the formation of the hydroxide monohydrate, in the final product the molar ratio of the ozonide and hydroxide should be equal to 2:1. This means that in ozonized sodium hydroxide, for example, the ozonide content content should be equal to 71% by weight, while in ozonized potassium hydroxide it should be 66.4% by weight. In the experiment, no more than 3–4% by weight \(\text{NaO}_3\) is detected in ozonized sodium hydroxide [6, 7], while no more than 4–5% by weight \(\text{KO}_3\) is detected in ozonized potassium hydroxide [8]. We were unable to reproduce the data cited in the article [9] on the formation of 63.5% by weight \(\text{KO}_3\) in ozonized potassium hydroxide in the reaction of ozone with KOH at 0°. The production of pure sodium and potassium ozonides is possible only when they are extracted from the ozonized alkalies with liquid ammonia. This is evidence that the reaction of ozonation of alkali metal hydroxides occurs chiefly on their surface. Consequently, the primary elementary events in the mechanism of ozonide formation should be associated with the reactions of heterogeneous catalytic decomposition of ozone.
The catalytic decomposition of ozone in the surface of KOH occurs very intensively according to the data of [10], especially at a positive temperature. Schwab, investigating the catalytic decomposition of ozone on the surfaces of a number of oxides [10], arrived at the conclusion that this process obeys the scheme

$$O_3 + \text{catalyst} \rightarrow O_2 + \text{catalyst}$$  \hspace{1cm} (6)

Ozone decomposes into molecular and atomic oxygen. Atomic oxygen is fixed on the catalyst surface. The number of gram atoms of oxygen formed in the decomposition of ozone should be equal to the number of gram molecules of the ozone decomposed; however, in the decomposition of m moles of ozone, the catalyst does not necessarily fix all the atoms of oxygen [10]. The number of moles of oxygen formed in the decomposition of ozone also should be equal to the number of moles of ozone decomposed. This is not observed in reaction (5), where 3.5 moles of oxygen and five gram atoms of oxygen (bonded in the form of 2MO₂) are formed in the decomposition of four moles of ozone.

To establish whether the decomposition of ozone on the surface of KOH, at positive temperature (40°) as well as negative temperatures, proceeds through the formation of an intermediate complex KOH · O₃ according to reactions (1) and (2) or according to scheme (6), we used an isotopic method. If we conduct the reaction of ozonation of oxygen-labeled K¹⁸OH with ozone of the natural isotopic composition, if reactions (1) and (2) are correct, we should not detect the heavy isotope of oxygen in the ozonide formed, since, according to [1, 2], the decomposition of the complex MOH · O₃ (reaction 2) proceeds according to the scheme

$$^16M^18OH + ^16O^18O^18O + ^16O_2 \rightarrow ^16M^18O_3 + ^16H^18O^18O + ^16O_2$$

This will be correct even if there is a rapid exchange of oxygen

$$^16M^18OH \cdot ^16O^18O^18O \rightarrow ^16M^18OH \cdot ^16O^18O^18O$$

We find the label only in water and in the oxygen formed in the recombination of hydroperoxyl 2H₂O₂* + H₂O* + 1.5O₂* (reaction 3). If, however, we detect K¹⁸O in the ozonide, then a different reaction, and not reactions (1) and (2) should be responsible for the formation of the latter at positive temperatures.

As can be seen from Table 1, our isotopic analysis of the oxygen of potassium ozonide, synthesized from K¹⁸OH and ozone of the natural isotopic composition is evidence that the hydroxide oxygen participates in the formation of the ozonide.

Samples of oxygen for the isotopic analysis of KOH were obtained by its reaction with mercuric chloride, followed by thermal decomposition of the mercuric oxide formed. Samples of oxygen for the isotopic analysis of KO₃ were obtained by its stepwise thermal decomposition to KO₂ and K₂O. According to the data of [11], at 60° potassium ozonide decomposes according to the reaction KO₃ → KO₂ + 0.5O₂. We arbitrarily call this oxygen the "ozonide" oxygen. The residue of KO₂ was decomposed at 415°, according to [12], to K₂O according to the reaction 2KO₂ → K₂O + 1.5O₂. We arbitrarily call this oxygen "superperoxide" +"peroxide," since the decomposition of the superperoxide to the oxide proceeds through the intermediate formation of the peroxide. Samples of oxygen from K₂O were also obtained by its reaction with mercuric chloride. This oxygen was arbitrarily called "oxide."

Thereby it was demonstrated that reactions (1) and (2) in the mechanism proposed by the authors of the articles [1, 2] evidently hold true only at negative temperatures.

It seems more probable to us that atomic oxygen is responsible for the formation of ozonides in the reaction of ozone with solid alkalies. The mechanism that we are proposing for the formation of ozonides provides for the successive occurrence of the following reactions

$$3O_2 + 2KOH \rightarrow 3O_2 + 2KOH \cdot O + 0$$  \hspace{1cm} (7)
$$2KOH \cdot O + O \rightarrow 2KO₂ + H₂O$$  \hspace{1cm} (8)
$$2O_2 + 2KO₂ \rightarrow 2KO₂ \cdot O + 2O_2$$  \hspace{1cm} (9)
$$2KO₂ \cdot O \rightarrow 2KO₂$$  \hspace{1cm} (10)
$$5O_3 + 2KOH \rightarrow 5O₂ + 2KO₂ + H₂O$$  \hspace{1cm} (11)